

The effect of composition of etchants on reactivity at line defects in antimony

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Abstract : The (111) cleavages of antimony single crystals were etched in the etchants containing citric acid, nitric acid and distilled water. Two different types of etching solutions were selected, in one type of etchant, the composition of citric acid was increased systematically, whereas in the other type of etchant, the composition of citric acid was increased and at the same time the composition of nitric acid was decreased correspondingly to maintain the total composition constant. The values of activation energy and frequency factor were calculated using Arrhenius law. The activation energy and the frequency factor vary in a different manner in both types of etchants. The results are explained.

Keywords : Etchants, line defects, activation energy

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1. Introduction

Considerable interest has been shown by various experimentalists to study the dislocation etching on (111) cleavages of antimony [1–3]. Recently, Raval and Joshi [4] studied the etching of antimony cleavages in citric acid containing etchants and Raval *et al* [5] with dextro tartaric and levo tartaric acid containing etchants. It is usually difficult to devise any simple classification for the components in the dislocation etchants. Broadly speaking, the etching solution can be of the following nature : (1) The primary requirement is an oxidising system to provide a thermodynamic 'driving force' to dissolve metal. The driving force is measured by the oxidation potential and which can be controlled by various ways, such as, the choice and concentration of the oxidant and concentration of the auxiliary reagents, *i.e.*, complexing agents. (2) Various factors can influence differently the effect of the oxidative driving force on different regions of the surface by controlling the activation energies of dissolution. Differential adsorption is an important factor and the choice of substances used in the oxidising system will depend on their adsorption behaviour.

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In this study, the authors have chosen various concentrations of nitric acid and citric acid in the etchant in order to study the role of different components in the etchants.

2. Experimental techniques and results

Single crystals of antimony were grown by modified Chalmer's technique which is described in detail elsewhere [6]. Metal of 99.999% purity was obtained from Nuclear Fuels Complex, Hyderabad, India. Many crystals were grown under temperature gradient of $92^{\circ}\text{C}/\text{cm}$ and growth velocity of 1.5 cm/hr . The crystals were cleaved at liquid nitrogen temperature in conventional way.

Two different sets of etchants were selected. In Etchants (A), the composition of nitric acid and distilled water was kept constant and citric acid composition was increased; whereas in the Etchants (B), the total composition of the etchant was kept constant and the citric acid composition was increased and at the same time, the nitric acid composition was decreased in equal amount. All the etchants produced triangular crystallographically oriented etch pits revealing $(111)[10\bar{1}]$ type dislocations. Table 1 shows the composition of etchants used.

Table 1. The values of activation energy and frequency factor for different etchants

Etchant	Composition of etchants	Etching time seconds	Activation energy eV	Freq Factor cm/sec
A	8 c.c Citric Acid + 3 c.c HNO_3 + 1 c.c distilled H_2O	75	1.16	1.88×10^{13}
	9 c.c Citric Acid + 3 c.c HNO_3 + 1 c.c distilled H_2O	105	0.73	7.70×10^5
	10 c.c Citric Acid + 3 c.c HNO_3 + 1 c.c distilled H_2O	30	0.46	4.42×10^2
	9 c.c Citric Acid + 3 c.c HNO_3 + 1 c.c distilled H_2O	105	0.73	7.70×10^5
	9.5 c.c Citric Acid + 2.5 c.c HNO_3 + 1 c.c distilled H_2O	26	0.63	1.77×10^5
	10 c.c Citric Acid + 2 c.c HNO_3 + 1 c.c distilled H_2O	75	0.74	8.84×10^6
B	9 c.c Citric Acid + 3 c.c HNO_3 + 1 c.c distilled H_2O	105	0.73	7.70×10^5
	9.5 c.c Citric Acid + 2.5 c.c HNO_3 + 1 c.c distilled H_2O	26	0.63	1.77×10^5
	10 c.c Citric Acid + 2 c.c HNO_3 + 1 c.c distilled H_2O	75	0.74	8.84×10^6
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	10 c.c Citric Acid + 2 c.c HNO_3 + 1 c.c distilled H_2O	75	0.74	8.84×10^6

The effect of composition of etchants on reactivity etc

Plate I



Figure 1. Photomicrograph showing the type of etch-pits produced on (111) cleavage plane of antimony single crystals by etching in the etchant containing 8 parts citric acid, 3 parts nitric acid and 1 part distilled water at 45°C for 75 sec. etching time.

The etching was carried out from room temperature to 55°C. It was also confirmed through various tests that these etchants revealed dislocations [7]. Figure 1 shows the type of etch pits produced by etching in the etchant containing 8 parts citric acid + 3 parts nitric acid and 1 part distilled water at 45°C.

The activation energy for lateral motion of ledges and the frequency factor can be found out by Arrhenius law [4]. Figure 2 shows the plot of logarithm of average width of etch pits W , versus the reciprocal of absolute temperature $1/T$, for the etchant containing 8 parts citric acid, 3 parts nitric acid and 1 part distilled water. The values of activation energy and frequency factor are listed in Table 1 for different etchants.

3. Discussion

Ogg [8] experimentally confirmed the conclusions of James and Turnstall [9] that the unit rhomb of antimony is 6.20 Å. The structure consists of two interpenetrating face-centered lattices. The shortest distances between the centres of the two atoms was found to be 2.92 Å. Lampert and Reichelt [10] described the crystal lattice of antimony having point group

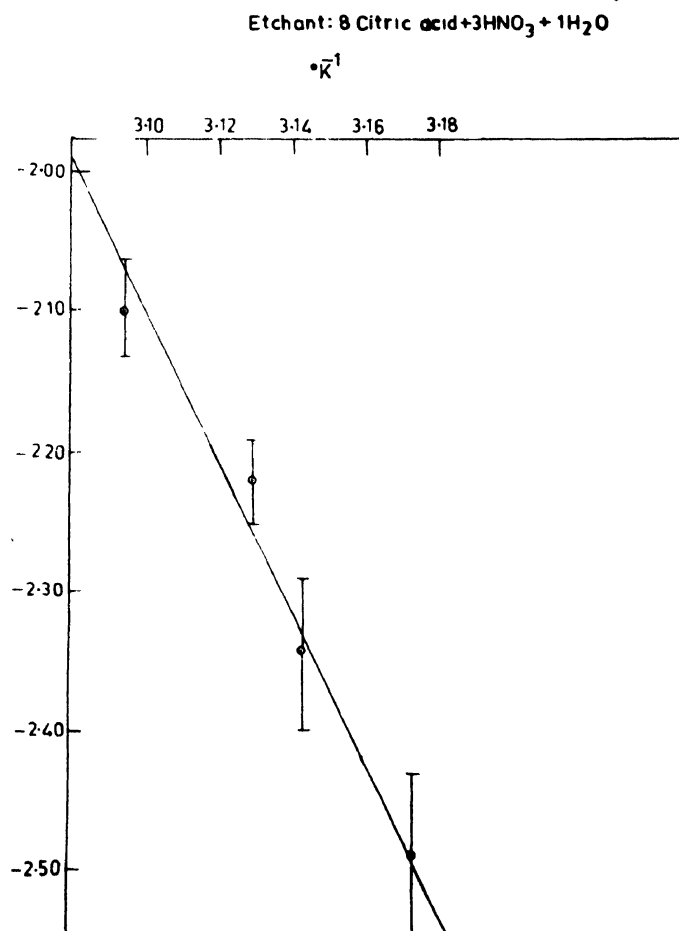


Figure 2. A plot of logarithm of average width of etch pit W versus $1/T$ for the etchant containing 8 parts citric acid, 3 parts nitric acid and 1 part distilled water

$R\bar{3}m$ and it is isomorphous to arsenic. They have illustrated the rhombohedral and hexagonal unit cell of antimony with the lattice consisting of double layers of atoms vertical to the $[111]$ directions. Each atom has three next neighbours in its own double layer and three second next neighbours in the adjacent layers. Atoms within the hexagonal plane are third next neighbours. Within the double layers, the bonds between the antimony atoms are mainly covalent, whereas between neighbouring double layers, Van der Waal bonds prevail.

The growth and dissolution of crystal is due to advance or retreat of monomolecular steps on the surface of the crystal $[11]$. The active sites are the places along the steps where single molecular rows end. These are known as 'kinks', where individual molecules can be deposited or removed. When a perfect face is exposed to a solvent, dissolution probably starts by the nucleation of unit pit of one molecular depth. These unit pits grow as steps retreat across the crystal through the action of kinks. This process is discussed in detail by Gilman *et al* $[12]$.

Rosenblatt and Lee $[13]$ and Rosenblatt $[14]$ reported the vapourization behaviour of antimony and found that the vapour of antimony is composed of mainly Sb_4 . The rate of antimony vapourization was found to be limited by the rate of kink initiation in straight-edge segments, but where the kink initiation rate was rapid enough compared to the rate of the kink motion and to the length of the ledges so that the number of kinks initiated along a given length of the ledge was proportional to the length of that ledge. Angus and Dyble $[15]$ proposed an etching model for (111) diamond surface, which includes the 'multiple kink mechanism'. Results of Lampert and Reichelt $[10]$ corresponds to that of Rosenblatt and Lee $[13]$.

Table 1 shows that in Etchants (A), as the composition of citric acid increases in the etchants, the values of activation energy and the frequency factor decrease. The activation energy can be thought of as a barrier to the reaction, therefore, the greater is the activation energy, slower is the rate of reaction. Hence, the increase in the composition of citric acid suggests faster rate of reaction. The values of the activation energy and frequency factor differ from the earlier cited values $[4]$ due to non-consideration of etch pits not corresponding to dislocations.

From Table 1, it is seen that in Etchants (B), the total composition of the etchants is maintained constant, *i.e.*, as the citric acid composition is increased, the composition of nitric acid is decreased accordingly. Increasing the concentration of citric acid decreases the activation energy and the frequency factor, thereafter again the values of activation energy and frequency factor increase with citric acid composition. This indicates the presence of a critical point which shows a deviation in the normal trend of reaction. This behaviour was reported in bismuth by Shah *et al* $[16,17]$ and recently by Raval *et al* $[5]$ in antimony. The nitric acid is serving as an oxidising agent in the composition of the etchants $[18]$, the variation in its composition seems to modify the kink kinetics in the ledges within the

etch-pits which has been reported earlier by Shah *et al* [16], responsible for deviation in the normal trend in Etchants (B).

4. Conclusions

- (1) All the etchants reveal dislocations of (111) $[10\bar{1}]$ type.
- (2) Increasing the composition of citric acid in the etchants (Etchants-A), the activation energy and the frequency factor decrease suggesting a lower barrier to be surmounted to form products and hence higher the reaction rate.
- (3) Increasing the composition of citric acid and decreasing the composition of nitric acid in the constant composition of etchants (Etchants-B), a critical point is observed where a deviation in normal behaviour is observed which corresponds to the earlier results in bismuth and antimony. This suggests that a specific composition of nitric acid is responsible for this behaviour with comparison to Etchants-A. This further suggests a modification in kink kinetics in the ledges within the etch pits.

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